

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Polyvinyl Fluoride and the continuous preparation thereof

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the continuous production of polyvinyl fluoride.

Vinyl fluoride homopolymers have been described in the prior art but have been unsatisfactory for industrial use in the production of films either because of difficulties encountered in processing them into film form or because such polymer as are readily convertible into films give films having little resistance to degradation caused by weathering.

The present invention provides vinyl fluoride polymers in which these disadvantages have, at least to a large extent, been overcome.

It has now been discovered that novel polyvinyl fluorides which are very suitable for use in the production of films are characterised by (1) a Solubility Index at 25° to 30° C. in hexamethylphosphoramide of less than 100, (2) a Melt-Flow Number in the range 5.0 to 10.0, (3) an Organosol Viscosity Index in the range 53 to 73, (4) an Amidine Number not greater than 0.40, and (5) in film form, an Accelerated Weatherability of at least 250 hours.

These novel polyvinyl fluorides can be made by a continuous process involving the free radical catalysed polymerisation of vinyl fluoride, which comprises continuously introducing into a reaction zone in which a pressure above 2000 pounds per square inch is maintained vinyl fluoride, water, and an initiator, α,α' -azo-bis(isobutyramidine hydrochloride), the weight ratio of vinyl fluoride to water being between 1:3 and 1:20, maintaining the contents of the reaction zone in a

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uniformly dispersed state, and continuously removing a slurry of polyvinyl fluoride in water from the reaction zone, the rates at which the reactants are introduced and the slurry is withdrawn being so controlled that the content of solid polyvinyl fluoride in the reaction zone is kept between 2% and 15% of the combined weight of water and polyvinyl fluoride, the temperature in the reaction zone and the content of the initiator in the water being selected substantially in accordance with the graph of the accompanying drawing. The resulting polyvinyl fluoride can be isolated from the slurry by any desired conventional separation and purification technique, e.g., by filtration, centrifuging, or the like, washing, and drying.

Vinyl fluoride monomer to be used as the starting material may be obtained by the hydrofluorination of acetylene according to the process described in United States Patent No. 2,118,901 or by the dehydrofluorination of 1,1-difluoroethane (which may be prepared according to procedures described in United States Patent No. 2,118,901 and British Specification No. 619,395) by any of several processes described in Specification No. 619,394 and United States Patents Nos. 2,480,560 and 2,674,632. Oxygen and acetylene are generally undesirable impurities, and it is preferable that neither be present to the extent of more than 1,000 parts by weight per million parts by weight of vinyl fluoride. α,α' -azo-bis(isobutyramidine hydrochloride) is also known as 2,2'-diguanyl-2,2'-azopropane dihydrochloride. Procedures for its manufacture are described in United States Patent No. 2,599,299.

The polymerisation is carried out at pressures in excess of 2,000 pounds per square inch. (Pressures are given throughout this specification as gauge pressures). The maximum pressure which may be used is dictated only by the limitations of available pressure equipment, and/or by economic considerations.

When the weight ratio of monomer to

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water is greater than 1:3, conversion of monomer to polymer becomes prohibitively low and recovery problems attendant on recycling unconverted monomer greatly increase. Below a ratio of 1:20, not enough monomer is provided at the reaction site to produce the more attractive, higher molecular weight polymers of which the process combination of temperature, pressure and initiator is capable.

Below 2% polymer solids in the reactor, the amount of water per pound of polymer produced which must be pumped to polymerisation pressure and thereafter separated from the polymer renders the process unattractive economically. Above 15% polymer solids in the reactor, the continual removal from the reactor of a uniform slurry becomes increasingly difficult and the risks of untimely termination of the continuous process due to plugging of the reactor or its valving are increased.

The accompanying drawing is a graph of temperature against initiator concentration on which are indicated the combinations of these two parameters which are usable in the process of the invention.

Referring to the drawing, for any given polymerisation pressure, within the operating area bounded by lines A and B and the appropriate Pressure Line are found combinations of polymerisation temperature and initiator concentration which when employed according to the invention produce the new and improved homopolymers of vinyl fluoride having the hereinbefore described properties. For the sake of clarity Pressure Lines are shown only for pressures of 2000, 4000, 8000 and 12000 pounds per square inch. The Lines for other pressures can be obtained by interpolation or, in the case of pressures above 12000 pounds per square inch, by extrapolation (the normal methods of interpolation or extrapolation on a log scale being applied). It should of course be borne in mind that the essential thing is that the polyvinyl fluoride produced should have the specified characteristics, and it is this fact, rather than the calculated form of the extrapolated curve, which is important in determining the process conditions. The precise form of the Pressure Line has been determined by experiment for a number of representative pressures and it is of course possible to follow the same procedure for other pressures, but generally interpolated curves will give adequate directions for successful working.

Line A, drawn upward at 57° C. from 40 parts per million of initiator is a real and practical boundary of the operating areas which cover the operative values of the temperature and initiator concentration. When continuous polymerisations are attempted at temperatures below 57° C., the rate of polymer chain propagation and the decom-

position of initiator are so retarded that the amount of initiator required to maintain polymerisation rates at even barely acceptance levels is prohibitive.

Line B, extending from 57° C./40 parts per million of initiator to approximately 141° C./0.3 parts per million of initiator represents an approximate practical limitation further bounding the operating areas. At temperature/initiator concentration combinations below this line, the scavenging effect on the free radicals (liberated by the initiator) or even minute quantities of impurities in, for example, the monomer or feed water streams may result in erratic polymerisation rates and lead to lack of reproducibility in the polymer.

At temperature/initiator concentration combinations outside the operating area for any given polymerization pressure, i.e., above and/or to the right of the pertinent Pressure Line, the polymers produced are found to be deficient in weatherability and/or extrudability, i.e., the new polyvinyl fluorides hereinbefore described are not obtained.

The salient properties which characterize and distinguish the new vinyl fluoride homopolymers are determined by the following tests:

SOLUBILITY INDEX.

Polymers have been traditionally characterized by their inherent viscosities in certain solvents as an order of magnitude indication of their molecular size. However the polymers produced by the process of this invention have been found extremely difficult if not impossible to characterize meaningfully in this matter because of their lack of complete solubility at even the very small concentrations normally employed in inherent viscosity determinations. The following procedure was therefore devised to characterize them.

Dissolve (so far as possible) 0.0500 ± 0.0002 grams of dry (i.e., containing less than 0.2% water) finely powdered polymer in 50 ± 0.05 millilitres of hexamethylphosphoramide by heating in a glass test tube, with stirring, at 150° ± 2° C. for 30 minutes. (The hexamethylphosphoramide employed is previously purified by vacuum distillation to produce a thermally stable material as indicated by viscosity stability at 150° C.). Cool the solution to room temperature, i.e., a temperature in the range 25° to 30° C., centrifuge and decant to separate undissolved swollen polymer from the solution.

Wash the undissolved swollen polymer twice by agitating it in fresh purified hexamethylphosphoramide, centrifuge and decant, discarding the wash solution. Add methanol to extract the hexamethylphosphoramide from the swollen polymeric mass, thereby precipitating the polymer. Filter off the precipitated polymer through a sintered glass crucible and dry to constant weight at 100° C. and atmospheric pressure.

$$\text{Solubility Index} = \frac{(W_0 - W_1) \times 100}{W_0}$$

Where W_0 is the weight of the original polymer sample, and W_1 is the weight of the polymer in the crucible.

It will be obvious that the presence of an insoluble fraction in the polymers of this invention renders their characterization by inherent viscosity measurements of doubtful significance.

The polymers of this invention have Solubility Indices less than 100.

The presence of an insoluble fraction in the polymers of this invention may be expressed in another manner by stating that the maximum concentration of completely dissolved polymer in a solution in hexamethylphosphoramide prepared by the above-described procedure will always be less than 1.0 ± 0.005 milligrams of polymer per millilitre of hexamethylphosphoramide.

MELT FLOW NUMBER.

The Melt-Flow Number of a particular polyvinyl fluoride is the square of the average diameter in inches of a roughly circular film disc resulting from the pressing between two polished chromium-plated steel plates of a 1-inch diameter wafer consisting of 1.00 ± 0.01 grams of the polymer in a dried, particulate, compressed form for 5 minutes at $260^\circ \pm 1^\circ$ C. under a total load of 12,250 pounds. The polyvinyl fluorides of this invention have Melt-Flow Numbers in the range 5.0 to 10.0. Melt-Flow Numbers are determined according to the following procedure: 1.00 ± 0.01 grams of the particulate polyvinyl fluoride, dried to less than 0.2% water by weight, is transferred to the 1-inch diameter die of a Buehler Metallurgical Mounting Press, the plug inserted and the die pressed for a few moments at a load of about 5000 pounds. After releasing the load, removing and disassembling the die, the resulting polymer wafer is an inch in diameter and about 100 mils thick. The wafer is then centred between two polished chromium-plated steel plates, 5 inches by 8 inches by 0.020 inches thick, with corners and edges smooth. This assembly is centred between the platens of a "Carver" Laboratory Press, the temperature of the surface of the centre of each platen being maintained at $260^\circ \pm 1^\circ$ C. ("Carver" is a Registered Trade Mark). The Carver Press has 5-inch by 5-inch electrically heated platens and is rated for a load of up to 10 tons. The polymer wafer is then pressed for 5 minutes at this temperature under a load of 12,250 pounds as indicated by the load gauge pointer. As the polymer mass melts and increases in diameter, it is necessary to pump up the press periodically to hold the load constant. At the end of the 5 minute pressing period, the load is immediately released

and the plate-polymer-plate assembly is removed from the press and immersed quickly in cool water. After allowing the assembly to remain for several minutes under water, the plates are separated and the film disc removed, dried by blotting, and its diameter measured to the nearest 0.01 inch. If the film disc is irregular, eight diameters are measured and averaged arithmetically. The square of this diameter is the Melt-Flow Number of the polymer.

ORGANOSOL VISCOSITY INDEX.

The Organosol Viscosity Index of a polyvinyl fluoride is the percentage of solvent in a dispersion of the polymer in particulate form in a latent solvent therefor at which the dispersion has a Brookfield viscosity of 1500 centipoises when measured at 20 revolutions per minute with a No. 5 spindle while the temperature of the dispersion is in the range 25° C. to 30° C. The Organosol Viscosity Index is determined by the following procedure: 200 grams of dried particulate polyvinyl fluoride is added slowly to 200 grams of gamma-butyrolactone (latent solvent) in a Waring Blendor operating on "low" speed. When all of the polymer has been added to the solvent, the Blendor is operated for 3 minutes on "high" speed. The resulting dispersion is poured into a 600 c.c. beaker and the No. 5 spindle of a Brookfield Variable Speed Synchro-Lectric Viscometer is immersed in the dispersion to the immersion mark on the spindle and the viscometer operated at 20 revolutions per minute. The scale reading is recorded and translated into centipoises (Brookfield). If the Brookfield viscosity of this dispersion is not exactly 1500 centipoises at this dilution, the dispersion is poured back into the Waring Blendor, and incremental additions of either polymer or solvent are made to the dispersion in the Blendor, depending on whether the Brookfield viscosity of the original dispersion was less or greater than 1500 centipoises. The Blendor is operated briefly at "high" speed each time an addition of either polymer or solvent is made to the dispersion. After each addition, the Brookfield viscosity is again determined, additions of either polymer or solvent continuing until a Brookfield viscosity of exactly 1500 centipoises is achieved. The solvent content of the dispersion at this time, expressed as a percentage of the total weight of polymer plus solvent, is the Organosol Viscosity Index of the polymer. The polyvinyl fluorides of this invention have Organosol Viscosity Indices in the range 53 to 73.

ACCELERATED WEATHERABILITY.

The Accelerated Weatherability of a polyvinyl fluoride is expressed as the number of hours that a molecularly unoriented film prepared therefrom must be exposed to intense ultraviolet irradiation in a gaseous oxidative atmosphere at a temperature above normal

room temperatures before its elongation at break, expressed as a percentage of the original length of the test specimen, is reduced below 10%. The polyvinyl fluorides of this invention have an Accelerated Weatherability of at least 250 hours. The accelerated exposures are carried out in a test device constructed as follows: Ten 20-inch long "Westinghouse" (Registered Trade Mark) FS20/T12 Fluorescent Sun Lamps are secured in parallel arrangement with their respective longitudinal axes spaced equidistantly around the circumference of an 8-inch diameter cylindrical aluminium rack. Film samples to be tested, each 6 x 2.5 inches, are arranged in three parallel circular rows around the inside of a 15.5-inch diameter slotted cylindrical aluminium rack. This rack is disposed concentrically about the cylindrical rack of sun lamps, thus placing the film samples three inches away from the lamps at closest approach. The slotted rack is connected to a mechanical drive and mounted so that it rotates continuously about its longitudinal axis at the rate of 34 revolutions per minute. Each square centimetre of film receives approximately $2.50-2.60 \times 10^{-7}$ einsteins of ultraviolet light per minute of exposure. The above-described device is disposed concentrically within a 22-inch diameter aluminium cylinder, sealed except for inlet and outlet bleeds to ensure a continuous supply of fresh air, an inlet pipe to admit ozone and connections at top and bottom to a by-pass recirculating air duct. During exposure, air containing 250 ± 50 parts per million of ozone is continuously circulated through the test chamber at the rate of 200 cubic feet per minute by means of a fan located in the recirculating duct, the ambient temperature within the test chamber being maintained at $60 \pm 2^\circ$ C. by means of a recorder-controller regulating a resistance type electric heater housed in the recirculating duct. The ambient relative humidity is not controlled during the test exposure. To ensure uniformity of exposure of individual film samples, fluorescent sun lamps are replaced after 1000 hours of use on a staggered basis, so that one pair of sun lamps located diametrically opposite one another on the cylindrical rack is replaced with new lamps every 200 hours. Further, every 150-160 hours of exposure, each film sample is moved to a different row in the slotted cylindrical rack on a random basis. The measurements of elongation at break employed to detect the weatherability end-point are made initially and at intervals of 75 to 150 hours during a given exposure. A film sample to be tested, after conditioning for at least 24 hours at 23.5° C. and 50% relative humidity, is elongated in an "Instron" Tensile Tester at the rate of 100% elongation per minute until the sample breaks. ("Instron" is a Registered Trade Mark). The width of each test specimen is $\frac{1}{2}$ -inch and the initial jaw-to-jaw separation is 1 inch. The elongation is the percentage increase in the length of the sample at break. The elongation at break for any given exposure interval is the average of at least 8 determinations. To ensure reproducibility in determining the Accelerated Weatherability of a particular polyvinyl fluoride, the unoriented films exposed in the accelerated weathering device are made in a particular manner. Approximately 40 parts by weight of particulate polyvinyl fluoride (containing less than 0.1% water by weight), and 60 parts by weight of N,N-dimethylacetamide are mixed together in a Waring Blendor and the castability of the resulting dispersion evaluated qualitatively by visual inspection of its viscosity. Based on experience, adjustments to the viscosity are made in the form of additions to the dispersion of either particulate polymer or dimethylacetamide. Such adjustments play no part in the magnitude of the Accelerated Weatherability of the film finally produced and are required merely for convenience in producing a castable dispersion. This dispersion is then transferred to sand milling equipment such as that described in Specifications Nos. 686,234 (batch type equipment) and 810,065 (continuous type equipment). One specific form of sand milling equipment comprises a water-jacketed stainless steel cylinder, fitted with a screened orifice near the base. The screen has a United States National Bureau of Standards Sieve Number of 325. A rotatable $\frac{3}{8}$ -inch diameter shaft on which are mounted three $\frac{1}{4}$ -inch thick discs is centrally located within the cylinder. The shaft is connected to a $\frac{1}{2}$ horsepower electric motor. A quantity of carefully washed and dried "Ottawa sand," designated by National Bureau of Standards Sieve Numbers 20-30, is introduced into the cylinder, the quantity of sand being sufficient to occupy between approximately $\frac{1}{3}$ and $\frac{1}{2}$ of the free space in the cylinder. The shaft is rotated at about 1800 RPM for a few minutes, during which time an intimate mixture of sand, polyvinyl fluoride and dimethylacetamide is formed by the rotating discs and flows downward towards the orifice where the sand is restrained by the screen while the remainder of the dispersion is delivered into a receiver. Cooling water is circulated through the cylinder jacket to prevent any appreciable rise in temperature during mixing in order to prevent premature coalescence of the polymer particles due to the action of the dimethylacetamide. If necessary to produce a smooth dispersion, sand milling may be repeated once or twice. The resulting dispersion is deaerated by gentle agitation under a vacuum until evolution of air bubbles ceases. The deaerated dispersion is then cast onto a polished chromium-plated steel plate and doctored to a thickness

sufficient to produce a solvent-free film approximately 4 to 6 mils thick. The plate with the doctored dispersion is exposed for about 1 minute under and $\frac{1}{8}$ -inch away from a metal-coated borosilicate glass heating plate maintained at 260° C., which exposure time is sufficient to cause the polymer particles to coalesce, producing a solvent-containing film. The plate carrying this film is then placed in a circulating air oven for 5 minutes at 150° C. to volatilize the bulk of the remaining dimethylacetamide, following which the plate and film are quenched by immersion in cold water. After stripping the film from the plate, it is clamped in a frame and exposed for 15 minutes in a circulating air oven at 150° C. to remove the remaining solvent. Plate-cast films containing more than 0.2% dimethylacetamide by weight, based on the total weight of polymer+solvent, are not employed in characterization testing.

AMIDINE NUMBER.

The Amidine Number of a polyvinyl fluoride is given by the relative intensities of two bands in the infrared absorption spectrum of a molecularly unoriented film plate cast from this polymer in the manner described for the preparation of films for the Accelerated Weatherability test. A particularly useful process for converting the polyvinyl fluorides of this invention into films comprises feeding mixtures comprising particulate polyvinyl fluoride and a latent solvent therefor into a heated extruder connected to a slotted casting hopper from which issues a latent solvent-containing polymer melt. As Amidine Number increases, the rheological compliance of such latent solvent-containing polymer melts increases. This leads to undesirable viscoelastic behaviour on extrusion, resulting in the production of extrudates having grossly roughened and deformed surfaces. The polyvinyl fluorides of this invention have Amidine Numbers not greater than 0.40, and do not exhibit these rheological deficiencies. Amidine Numbers are determined by the following procedure: The infrared absorption spectrum of the film from 2.0 to 7.0 microns is recorded by a Perkin-Elmer Model 21 Infrared Spectrometer on absorbance (i.e., logarithmic) spectrometer chart paper. The height (H_1) of the absorbance shoulder at 3.72 microns (absorbance at this wave length being attributed to the carbon-fluorine bond which is proportional to film thickness for a homopolymeric vinyl fluoride film, is measured with reference to a convenient and reproducible

base line drawn connecting the absorbance minima near 3.0 and 5.0 microns respectively. The height (H_2) of the absorbance peak at 5.98 microns [absorbance at this wavelength being attributed to the amidine structure found in the initiator, α, α' -azo-bis-(isobutyramidine hydrochloride)], which is proportional to the amount of initiator fragments attached to the polymer, is measured with reference to a second convenient and reproducible base line drawn connecting the absorbance minima near 5.0 and 6.5 microns respectively. The Amidine

number is given by $\frac{H_2}{H_1}$, and is a measure of the concentration of initiator fragments attached to the polymer.

Any reaction vessel designed for high pressure synthesis may be employed in carrying out the process of this invention. Such a vessel, should, of course, be provided with stirring or agitating means for maintaining the contents thereof in a highly dispersed, substantially uniform state; and means should be provided for continuously metering reactants into the vessel, and for continuously removing the slurry of polymer therefrom, so as to maintain the contents of the reaction vessel within the limits above specified.

Examples summarised in Tables I and II illustrate the invention, Parts and percentages are by weight.

In each of the Examples a stream of filtered, deoxygenated, deionised water containing α, α' -azo-bis-(isobutyramidine hydrochloride) in the concentrations shown (in parts per million of water) and a stream of vinyl fluoride monomer were continuously fed at the indicated weight ratio of vinyl fluoride to water into a stainless steel reactor operating at the indicated pressure. The reactor was maintained at the specified temperature, and was provided with a high degree of agitation such that the contents were intimately mixed and substantially uniform from point to point within the vessel. The reactor pressure was maintained at the indicated value by automatically controlling the rate of product withdrawal through a valve which dropped the pressure of the effluent stream from reaction pressure to atmospheric pressure. The initiator concentration in the reactor was maintained at the value indicated in Table I. The slurry produced comprised finely particulate polyvinyl fluoride and water. The polymer was separated from the water and recovered as a substantially dry powder.

TABLE I
Polymerization Conditions

Example No.	Feed		Conditions in Reactor			
	Initiator — Concentration ppm. of water	Monomer-to- Water Weight Ratio	Press., psi	Temp., °C.	Initiator Conc., ppm. of water	Polymer Solids, % of Polymer/ Water Mixture
1	80	1:10.4	4,000	97	27	6.9
2	51	1:12	8,000	97	27	5.9
3	44	1:11.7	12,000	97	27	6.2
4	2220	1:7.6	4,000	77	2000	5.0
5	5800	1:5.9	4,000	77	5270	5.3
6	22	1:7.6	4,000	127	2.6	5.0
7	888	1:11.8	4,000	67	860	2.3
8	333	1:8.7	4,000	97	135	7.7
9	18	1:10	8,000	109	5	4.1
10	41	1:6.8	8,000	97	22	5.8
11	103	1:7.6	4,000	97	27	10.1
12	47	1:24	8,000	97	22	3.4
13	97	1:10.2	1,600	97	27	4.6

TABLE II
Characterization of Polymer

Example No.	Accelerated Weatherability, hrs.	Melt-Flow Number	Amidine Number	Organosol Viscosity Index	Solubility Index
1	320	7.3	0.20	60	78
2	450	6.8	0.18	61	86
3	590	6.5	0.15	63	88
4	330	6.3	0.70	74	75
5	140	8.0	2.10	77	90
6	195	10.6	0.19	69	32
7	360	6.4	0.27	72	84
8	230	8.4	0.40	64	77
9	420	7.3	0.20	63	96
10	500	6.7	0.17	63	90
11	330	7.4	0.22	61	72
12	200	9.0	0.20	64	75
13	230	8.3	0.36	63	73

It will be evident from the results set forth in Table II, that, as previously stated, in order to secure the novel and improved vinyl fluoride homopolymer of this invention, it is essential that the prescribed limitations which define the process of this invention be observed. Thus, in Examples 4, 5 and 6 the concentrations of reaction initiator maintained in the reactor (Table I) falls outside the operating area for the pressure employed, and, as a consequence, the polymer produced in each case is too low in weatherability, and/or of extremely poor extrudability, and/or is not satisfactorily dispersible. In Example 8 the concentration of initiator is just outside the operating areas for a pressure of 4000 psi; the resulting product has an Amidine Number of 0.40 and is therefore of borderline extrudability, weatherability is just slightly below the acceptable level, and dispersability is just within the acceptable range. Example 12 demonstrates that too low a monomer-to-water ratio in the feed to the reactor, results in a less weatherable polymer, of lower molecular weight even though initiator concentration and temperature are within the operating area for the 8000 psi pressure maintained in the reactor. Similarly, as shown in Example 13 too low a polymerization pressure results in a polymer of low weatherability.

WHAT WE CLAIM IS:—

1. A homopolymer of vinyl fluoride having a Solubility Index at 25° to 30° C. in hexamethylphosphoramide of less than 100, a Melt-Flow Number in the range 5.0 to 10.0, an Organosol Viscosity Index in the range 53 to 73, an Amidine Number not greater than

0.40, and, in film form, an Accelerated Weatherability of at least 250 hours.

2. A continuous process for the production of a homopolymer of vinyl fluoride as claimed in Claim 1 by the free radical catalysed polymerisation of vinyl fluoride, which comprises continuously introducing into a reaction zone in which a pressure above 2000 pounds per square inch is maintained vinyl fluoride, water and as initiator, α, α' -azobis(isobutyramidine hydrochloride), the weight ratio of vinyl fluoride to water being between 1:3 and 1:20, maintaining the contents of the reaction zone in a uniformly dispersed state, and continuously removing a slurry of polyvinyl fluoride in water from the reaction zone, the rates at which the reactants are introduced and the slurry is withdrawn being so controlled that the content of solid polyvinyl fluoride in the reaction zone is kept between 2% and 15% of the combined weight of water and polyvinyl fluoride, and the temperature in the reaction zone and the content of the initiator in the water being selected substantially in accordance with the graph of the accompanying drawings and so that a vinyl fluoride homopolymer of the defined properties is obtained.

3. A continuous process for the production of polyvinyl fluoride according to Claim 2, substantially as hereinbefore described.

4. Polyvinyl fluoride obtained by a process claimed in Claim 2 or 3.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

